SU(2) instantons with boundary jumps and spin tunneling in magnetic molecules

Ersin Keçecioğlu and Anupam Garg*
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208

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Coherent state path integrals are shown in general to contain instantons with jumps at the boundaries, i.e., with boundary points lying outside classical parameter or phase space. As an example, the magnetic molecule Fe_8 is studied using a realistic Hamiltonian, and instanons with jumps are shown to dominate beyond a certain external magnetic field. An approximate formula is found for the fields where ground state tunneling is quenched in this molecule.

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The purpose of this paper is to discuss two problems, a specific one and a general one. The specific problem concerns the tunneling between ground Zeeman levels of certain magnetic molecules [1]. The general problem concerns the nature of tunneling paths, or instantons, in coherent state or phase space path integrals [2]. As a rule, such paths can be found only if one complexifies phase space, i.e., allows either the momenta, or the coordinates, or both, to become complex. However, in all previous studies of which we are aware, the instantons always start and end in real phase space, at the points corresponding to the classical energy minima. The new instantons reported here, by contrast, do not even have end points in real phase space. We refer to these as boundary jump instantons. Such paths are a basic part of the formal structure of coherent state and phase space path integrals [3, 4], but there has never been a need to include them in tunneling problems, as paths without jumps have always been available [5]. This, as we shall show, is not an accident. Boundary jump instantons are analogous to extra saddle points in the method of steepest descents for one-dimensional integrals, and like them, may or may not be relevant in any given situation. But, one can not ignore them a priori. In this paper we give the rules for finding these extra paths and their contribution to tunneling, and apply them to our illustrative example.

Our work is part of the broader program of studying the semiclassical limit of spin systems. Tunneling is just one of the phenomena amenable to semiclassical methods. Many problems, from rotating molecules to many-body aspects of nuclear structure, can be modelled in terms of a large spin, for which the semiclassical approximation is the natural one [6]. It is perhaps not widely realized that this limit is not as well understood for spin as it is for massive particles. The correct semiclassical spin propagator has been recognized only gradually since the late 1980's [7], and its consistency under composition of successive propagators was shown only recently [8].

We begin by describing our specific problem. The molecular ion $[(\mathrm{tacn})_6\mathrm{Fe}_8\mathrm{O}_2(\mathrm{OH})_{12}]^{8+}$ (or just Fe_8 for short) forms a solid in which the Fe_8 groups are essentially noninteracting, and each behaves like a single spin of magnitude $J = 10$ in its ground manifold. The degeneracy of the 21 Zeeman levels is partly lifted by spin-orbit effects. Including an external magnetic field, the system is well described by the anisotropy Hamiltonian [9]

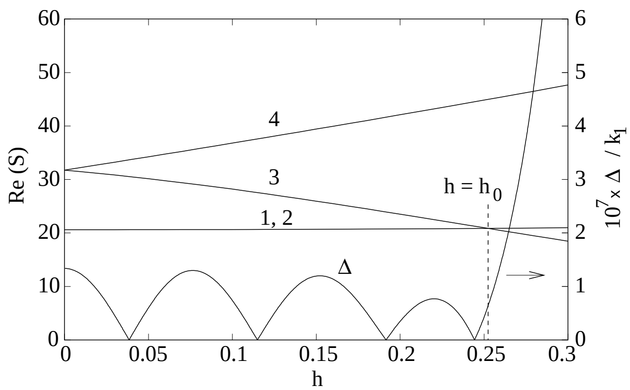

FIG. 1: Re S for the Fe_8 instantons, marked 1–4 as shown. S_3 and S_4 are purely real. Also shown is the ground pair splitting $\Delta(h)$.

$$\mathcal{H} = k_1 J_z^2 + k_2 J_y^2 - C[J_+^4 + J_-^4] - g\mu_B J_z H, \qquad (1)$$

where $\mathbf{J} = (J_x, J_y, J_z)$ is a spin operator, and $J_\pm = J_z \pm iJ_y$ (not $J_x \pm iJ_y$). If $H = 0$, the spin has degenerate classical minima along the $\pm\hat{\mathbf{x}}$ axes, which cant symmetrically toward $\hat{\mathbf{z}}$ as H is turned on. We wish to study the splitting Δ due to quantum tunneling between these minima, particularly as a function of H. It is convenient to work in reduced variables $\lambda = k_2/k_1$, $\lambda_2 = CJ^2/k_1$, and $h = H/H_c$, with $H_c = 2k_1 J/g\mu_B$. Measurements yield $g \simeq 2$, $k_1 \simeq 0.338$ K, $k_2 \simeq 0.246$ K, and $C \simeq 29\,\mu$K [1, 10].

The splitting $\Delta(H)$ oscillates with H, being quenched at certain H [11, 12]. The effect can be viewed in terms of two instantons that wind about the hard axis, $\hat{\mathbf{z}}$, in opposite directions, and interfere with one another [13]. Their actions differ by $iJ\mathcal{A}$, where $\mathcal{A}$ is a real Berry phase equal to the area of the closed loop formed by the two paths on the complexified unit sphere. $\Delta(H) = 0$ whenever $J\mathcal{A}(H)$ is an odd multiple of π. If $C = 0$, there are $2J$ quenching fields, at $H = (J - n - 1/2)\Delta H$, with $n = 0, 1, \ldots, 2J-1$, and $\Delta H = (1-\lambda)^{1/2} H_c/J = 0.263$ T.

Turning on even a small C has a big quantitative effect. With the value for Fe_8, e.g., direct numerical diagonalization of $\mathcal{H}$ (see Fig. 1) reveals only 4 quenching points for $H > 0$ instead of 10. The spacing remains quite regular, but is increased by $\sim 50\%$. Given the visual appeal of the interfering instanton picture, it is interesting to ask how this picture is modified when $C \neq 0$. To this end, we review some aspects of SU(2) instantons.

In the instanton method, one seeks a propagator such as $K_{fi} = \langle z_f | \exp[-\mathcal{H}T] | z_i \rangle$ via the path integral

$$K_{fi} = \int d[z] d[\bar{z}] e^{-S(\bar{z}(t), z(t))} \tag{2}$$

in the limit $T \to \infty$. Here, $|z_{i,f}\rangle$ are (unnormalized) spin coherent states defined for any complex number z by $|z\rangle = e^{zJ_-}|J, J\rangle$, where $|J, J\rangle$ is the eigenstate of $\mathbf{J}^2$ and J_z with eigenvalues $J(J+1)$ and J. Further, $\mathbf{J} \cdot \hat{\mathbf{n}} |z\rangle = J|z\rangle$, if $z = \tan(\theta/2) e^{i\phi}$, (θ, ϕ) being the spherical polar coordinates of $\hat{\mathbf{n}}$. We will take the points z_i and z_f to be degenerate minima of the classical energy. S is the action for a path specified by $z(t)$ and $\bar{z}(t)$, and is given by

$$S = -\int_{-T/2}^{T/2} \left[J \frac{\dot{\bar{z}} z - \bar{z} \dot{z}}{1 + \bar{z} z} - H(\bar{z}, z) \right] dt. \tag{3}$$

Here, z and $\bar{z}$ are formal complex conjugates, but should be regarded as independent variables, since both are needed to determine θ and ϕ, e.g. Further,

$$H(\bar{z}', z) = \langle z' | \mathcal{H} | z \rangle / \langle z' | z \rangle. \tag{4}$$

For $\mathcal{H}$'s such as (1) that are polynomial in J_i, $H(\bar{z}', z)$ is holomorphic in z and antiholomorphic in z' [14]. In Eq. (3), the first term is the Wess-Zumino or Berry phase term. We will refer to the two terms in S as the kinetic and dynamical terms, S_K and S_D.

Instantons are paths that start at z_i and end at z_f, and obey the Euler-Lagrange (EL) equations,

$$\dot{\bar{z}} = \frac{(1 + \bar{z} z)^2}{2J} \frac{\partial H}{\partial z}, \qquad \dot{z} = -\frac{(1 + \bar{z} z)^2}{2J} \frac{\partial H}{\partial \bar{z}}. \tag{5}$$

It is easily verified that along these paths energy is conserved, i.e., $dH(\bar{z}, z)/dt = 0$. Because of this, and because z_i and z_f are energy minima, one cannot find a solution lying on the real unit sphere. We must allow $\bar{z}$ and z to be completely independent complex variables. In other words, $\bar{z}(t)$ need not equal $z^*(t)$, where the star denotes the *true* complex conjugate. However, one can always find an instanton with endpoints on the real sphere. This is because, if we denote the minimum energy by $E_{\min}$, the instanton obeys $H(\bar{z}(t), z(t)) = E_{\min}$, and one clearly has $H(z_i^*, z_i) = H(z_f^*, z_f) = E_{\min}$.

Let us illustrate this using Eq. (1) with $C = 0$. Then,

$$H(\bar{z}, z) = k_1 J^2 \left[\frac{(1 - \bar{z} z)^2 - \lambda (z - \bar{z})^2 - 2h(1 - \bar{z}^2 z^2)}{(1 + \bar{z} z)^2} \right]. \tag{6}$$

The minima are at $\bar{z} = z = \pm z_0$ where $z_0 = [(1-h)/(1+h)]^{1/2}$, and $E_{\min} = -k_1 J^2 h^2$. From $H(\bar{z}, z) = E_{\min}$ we obtain $\bar{z}(z)$:

$$\bar{z} = \frac{\sqrt{\lambda} z \pm (1 - h)}{\sqrt{\lambda} \pm (1 + h) z}. \tag{7}$$

These equations give the instanton trajectories in z-$\bar{z}$ space, without giving the t dependence. For general z, $\bar{z} \neq z^*$, but if $z = \pm z_0$, $\bar{z} = z^*$. Thus the instanton endpoints are on the real sphere. From Eq. (7), we can now evaluate S, and recover previous results, along with the interference effect [11].

If we now turn on C, the solutions (7) will evolve smoothly, and continue to have classical end points. They will continue to interfere, and one can find the fields where Δ vanishes by calculating $J\mathcal{A}$ numerically. When we do this, we find that the spacing agrees closely with the answer from direct diagonalization of $\mathcal{H}$, but we also find, incorrectly, quenching points at $h > h_0 \simeq 0.25$.

The problem is that we have not formulated the principal of least action (or Hamilton principal function, to be precise) sufficiently carefully [3, 4, 8]. One must in fact include an explicit boundary term S_B in S:

$$S_B = J \ln \left[\frac{(1 + \bar{z}(-T/2) z_i)(1 + \bar{z}_f z(T/2))}{(1 + z_i^* z_i)(1 + \bar{z}_f \bar{z}_f^*)} \right]. \tag{8}$$

If we now vary $S = S_K + S_D + S_B$ *including the endpoints*, and set δS to 0, we discover of course the EL equations (5), but also that δS has no terms in $\delta \bar{z}(-T/2)$ and $\delta z(T/2)$. This means that the boundary conditions on Eq. (5) are

$$z(-T/2) = z_i, \quad \bar{z}(T/2) = \bar{z}_f, \tag{9}$$

and that $\bar{z}_i \equiv \bar{z}(-T/2)$ and $z_f \equiv z(T/2)$ must be left free. Otherwise, we would have four boundary conditions on a second order system of differential equations, and the problem would be overdetermined. The term S_B can also be found by careful time-slicing of the propagator. Its inclusion in S has many other nice consequences: e.g., the Hamilton-Jacobi equations

$$\frac{\partial S^{\rm cl}}{\partial \bar{z}_f} = 2J \frac{z_f}{1 + \bar{z}_f z_f}, \quad \frac{\partial S^{\rm cl}}{\partial z_i} = 2J \frac{\bar{z}_i}{1 + \bar{z}_i z_i}. \tag{10}$$

Since $\bar{z}_i$ and z_f are not determined, one may have solutions to Eqs. (5) and (9) with $\bar{z}_i \neq z_i^*$, $z_f \neq \bar{z}_f^*$. These are the boundary jump instantons. Their velocities $\dot{z}$ and $\dot{\bar{z}}$ do not vanish at the end points because the derivatives $\partial H/\partial z$ and $\partial H/\partial \bar{z}$ are not zero. Thus the instanton duration is finite, and although the energy $E = H(\bar{z}, z)$ is still a constant of motion, the value of E is not immediately obvious. In fact, since $S_D = \int H dt$, we must choose $E = E_{\min}$. Otherwise, when we sum multiinstanton terms, the instantons with jumps will trivially

dominate or be dominated by those without jumps. This point comes out more easily in Klauder's formulation. He argues that since the continuum path integral is a formal construct with meaning only as a limit of its discrete version, one may add a term to the integrand for S that is quadratic in the velocities $\dot{\bar{z}}$ and $\dot{z}$, with an infinitesimal coefficient ϵ that is sent to 0 at the end. The EL equations are then a fourth order system, and one may specify all four z_i, $\bar{z}_i$, $\bar{z}_f$ and z_f. The instantons with jumps then appear as solutions to the EL equations with internal boundary layers of thickness $O(\epsilon)$ since the terms in $\ddot{z}$ and $\ddot{\bar{z}}$ have coefficients ϵ. Energy is conserved in these boundary layers too, and when one takes the $\epsilon \to 0$ limit, they yield a contribution that is explicitly independent of ϵ (which makes the procedure legitimate), and is precisely equal to S_B above. Note that $S_B = 0$ for an instanton without jumps.

Hence the general procedure for finding all instantons is as follows. For any $\mathcal{H}$ with degenerate minima, we first find $E_{\rm min}$, and the classical minima (z_i^*, z_i), (z_f^*, z_f). We then find the allowed values of $\bar{z}_i$ by solving

$$H(\bar{z}, z_i) = E_{\rm min}. \tag{11}$$

This equation has a double root at $\bar{z} = z_i^*$, since

$$\left.\frac{\partial}{\partial \bar{z}} H(\bar{z}, z)\right|_{z_i^*, z_i} = \left.\frac{\partial}{\partial z} H(\bar{z}, z)\right|_{z_i^*, z_i} = 0. \tag{12}$$

However, it may also have additional roots at $\bar{z} \neq z_i^*$, which will then be the end points of instantons with boundary jumps. (A completely analogous procedure applies to z_f.) We then obtain $\bar{z}(z)$ for all instantons from energy conservation, making sure that they connect on to the appropriate end points. This is enough to compute S_K and S_B for each instanton (the time dependence is not needed), and $S_D = E_{\rm min} T$ for all of them. If we label the various instantons by α, we can write

$$\Delta = \sum_\alpha \gamma_\alpha e^{-S_\alpha}, \tag{13}$$

where γ_α is the prefactor arising from integrating over Gaussian fluctations about each instanton. On physical grounds we expect γ_α to be of the same order for all α for smooth Hamiltonians, and it may be estimated as the small oscillation frequency about the minimum. (For instantons without boundary jumps, Ref. [15] formulates how to find γ_α.) Hence, the relative importance of various instantons is determined largely by the actions S_α.

Let us now return to our model (1). It may be verified that $H(\bar{z}, z) = P(\bar{z}, z)/(1 + \bar{z}z)^4$, where P is a polynomial of degree 4 in $\bar{z}$ and also in z. Thus Eq. (11) is a quartic in $\bar{z}$. Two of its roots are indeed z_i^*, and connect on to instantons without jumps, but two are different and distinct and connect to instantons with jumps. The equation $H(\bar{z}, z) = E_{\rm min}$ is also a quartic and the solution

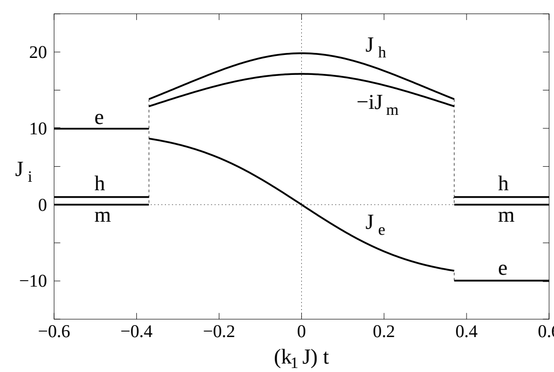

FIG. 2: A jump instanton (number 3), for $H = 0.1H_c$. Suffixes e, m, and h denote easy, medium, and hard axes.

$\bar{z}(z)$ has four branches, correpsonding to the different instantons. We label the first two instantons, which have Im $S \neq 0$, and interfere with each other, 1 and 2, and the last two, which have jumps and Im $S = 0$, 3 and 4. An instanton with a jump at one end also has a jump at the other end. A 180° rotation about $\hat{\mathbf{z}}$ sends instanton 1 into 2, which guarantees $\mathrm{Re}\, S_1 = \mathrm{Re}\, S_2$, $\gamma_1 = \gamma_2$. We show instanton 3 in Fig. 2, 1 and 2 in Fig. 3 (all for $h = 0.1$), and $\mathrm{Re}\, S_\alpha(h)$ in Fig. 1. For any h, the dominant instanton is that with the least $\mathrm{Re}\, S$. Hence, except in the immediate vicinity of h_0, only instantons 1 and 2 are relevant for $h < h_0$, and only 3 is relevant for $h > h_0$. This explains why Δ does not oscillate for $h > h_0$.

We can find the quenching fields numerically, but we have also found an analytic approximation, based on the small parameter $\zeta \equiv 4\lambda_2 h^2$, which explains why they are so regularly spaced. This result may also be of wider interest, since Δ oscillations have now been seen in another system [16]. To derive this, it is better to use polar coordinates. With $u \equiv \cos\theta$ and $s \equiv \sin\phi$, the energy

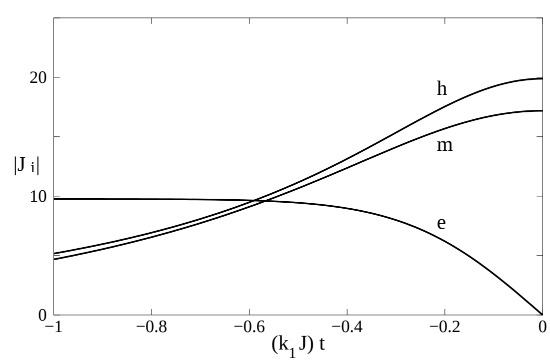

FIG. 3: Instantons without jumps for $H = 0.1H_c$. We show $|J_i|$, since now all J_i are complex. All $|J_i|$ are even about $t = 0$, and J_m slowly asymptotes to 0 as $t \to \pm\infty$.

conservation condition takes the form

$$g(u,s) = -\tfrac{1}{2}Z(s)u^4 + R(s)u^2 - 2hu + W(s) = 0, \quad (14)$$

where

$$\begin{aligned} Z(s) &= 4\lambda_2(1+6s^2+s^4), && (15)\\ R(s) &= 1-\lambda s^2 + 12\lambda_2 s^2 + 4\lambda_2 s^4, && (16)\\ W(s) &= g_0 + h^2 + \lambda s^2 - 2\lambda_2 s^4, && (17)\end{aligned}$$

with $g_0 = -(\lambda+h^2) - E_{\rm min} \approx 2\lambda_2 h^4$. $g(u,s)$ has four roots $u(s)$. Regarding s as real, we are interested in the complex conjugate pair of roots which tend to the energy minima $\theta=\theta_0$, as $s\to 0$. Let the real and imaginary parts of these roots be $A(s)$ and $B(s)$, i.e., let

$$u(s) = A(s) \pm iB(s). \quad (18)$$

From the imaginary part of Eq. (14) we get

$$B^2 = A^2 - (R/Z) + (h/AZ), \quad (19)$$

and if we substitute this result for B into the real part, we get an equation for A alone:

$$4Z^2A^6 - 4RZA^4 + (R^2+2WZ)A^2 - h^2 = 0. \quad (20)$$

We now make the self-consistently verifiable assumption that $A = O(h)$. Then the terms ZA^4 and Z^2A^6 are $O(\zeta)$ and $O(\zeta^2)$ relative to the the remaining terms, and may be dropped. This yields $A = h(R^2+2WZ)^{-1/2}$. The quantity R^2+2WZ can be seen to be a fourth order polynomial in s, and depends on h only through the combination $\lambda_2(h^2+g_0)$, which is $O(\zeta)$. If we neglect this weak h dependence, we get

$$\begin{aligned} A(\phi) &\approx h(1+P_2\sin^2\phi + P_4\sin^4\phi)^{-1/2}, && (21)\\ P_2 &= -2\lambda + 24\lambda_2 + 8\lambda_2\lambda, && (22)\\ P_4 &= \lambda^2 + 8\lambda_2 + 24\lambda\lambda_2 + 128\lambda_2^2. && (23)\end{aligned}$$

Since $S_K = iJ\int(1-\cos\theta)\dot\phi\, dt$ in θ, ϕ variables, $\mathcal{A} = 2\pi - \int_0^{2\pi} A(\phi)d\phi$. If we keep only instantons 1 and 2, $\Delta = 2\gamma_1\exp(-{\rm Re}S_1)\cos(J\mathcal{A}/2)$ up to a phase factor. Using Eq. (21), we see that the zeros of Δ are equally spaced with spacing $\Delta H = \pi H_c/JI(\lambda,\lambda_2)$, where

$$I(\lambda,\lambda_2) = \int_0^\pi \frac{d\phi}{(1+P_2\sin^2\phi+P_4\sin^4\phi)^{1/2}}. \quad (24)$$

For the Fe_8 parameters, $I = 3.88$, implying $\Delta H = 0.409$ T. The experimental value is 0.41 T.

We conclude with some general remarks about instantons with boundary jumps (or internal boundary layers, in the Klauderian view). It is clear that they must be present in all coherent state path integrals, not just for spin, and our discussion is easily extended to these cases. It would be interesting to find other concrete instances where they occur, both in quantum mechanics, and in field theories. It would also be interesting to reexamine problems such as a particle in a one dimensional potential well in a coherent state formulation.

* e-mail address: agarg@northwestern.edu

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